

## PATENT COOPERATION TREATY

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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 24 MAR 2005

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10/531690

Applicant's or agent's file reference XXX	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/PL 03/00066	International filing date (day/month/year) 02.07.2003	Priority date (day/month/year) 21.10.2002
International Patent Classification (IPC) or both national classification and IPC C23C8/22		
Applicant SECO/WARWICK SP. Z O.O. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

- I  Basis of the opinion
- II  Priority
- III  Non-establishment of opinion with regard to novelty, inventive step and Industrial applicability
- IV  Lack of unity of invention
- V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI  Certain documents cited
- VII  Certain defects in the international application
- VIII  Certain observations on the international application

Date of submission of the demand 19.04.2004	Date of completion of this report 23.03.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Badcock, G  Telephone No. +49 89 2399-8445



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/PL 03/00066

## I. Basis of the report

- With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, Pages

1-4 received on 03.12.2004 with letter of 30.11.2004

### Claims, Numbers

4, 5 as originally filed  
1-3 received on 03.12.2004 with letter of 30.11.2004

- With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

- With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

- The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

- This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

- Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/PL 03/00066

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1-3
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-3
Industrial applicability (IA)	Yes:	Claims	1-3
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/PL 03/00066

**Novelty, Art.33(2) PCT and Inventive step, Art.33(3) PCT**

JP-A-2000001765 discloses a method of vacuum decarburization, in which a gas of 70% ethylene gas and 30% acetylene is used, (cf. [0024]). The mixture of claim 1 is novel since the disclosed acetylene to ethylene ratio is, therefore, 0.428 - which is below the claimed lower limit of 0.5. However, claim 1 is directed to a gas mixture per se. The gas mixture is only alleged to demonstrate a surprising effect when used in a process of under pressure carburizing. It has neither been alleged, nor demonstrated, to have a surprising effect pe se over its entire scope. Therefore, since the mixture is not limited to use in a method of low pressure carburizing, it does not have an inventive merit over its full scope. The mixture of claim 1 is not inventive.

The same applies in principle to the preferred features in claims 2-3.

## Hydrocarbon gas mixture for the under-pressure carburizing of steel

The object of the present invention relates to a mixture used in vacuum furnaces for under-pressure carburizing of steel products, mainly parts of machines, vehicles and all sorts of mechanical apparatuses.

From the US Patent 5,702,540 a process is known, in which a charge is processed under vacuum in the presence of a carbon carrier which consists of unsaturated aliphatic hydrocarbons, where the pressure in the chamber shall not be higher than 1 kPa.

Another US Patent, 6,187,111, uses gaseous ethylene as the carbon carrier and the pressure in the chamber shall be within the range of 1 to 10 kPa, whereas the charge shall have the temperature between 900°C and 1100°C.

The patent EPO 0,882,811 is also known in which the carbon carrier is a hydrocarbon with a strict 1:1 carbon-to-hydrogen ratio.

To obtain the required carburizing result the carbon carrier, ethylene or acetylene, is introduced to a hot vacuum furnace chamber during the carburizing stage either in a continuous or a pulse manner. The carbon carrier can be introduced together with other chemically inert gases, e.g. nitrogen, argon, or active gases, e.g. hydrogen, in order to control the efficiency and cleanliness of the carburizing process, as well as with active nitrogen carriers, e.g. ammonia, for carbonitriding of steel.

The main point and essence of the present invention is the mixture for under-pressure carburizing, ensuring decomposition of 70% to 90% of hydrocarbons. The mixture consists of the carbon carrier, containing acetylene and ethylene; while the acetylene to ethylene ratio is within the range between 0.5 and 2.0.

2.

Moreover, the carbon carrier is mixed with hydrogen or with ammonia. In the case of mixing the carbon carrier with hydrogen, volume ratio 0.7 to 1 should be maintained. For ammonia this ratio is 0.7 to 5.0.

The mixture according to the present invention is characterized by the effect of synergy of uniform carburizing of intricate shape workpieces, especially those with narrow and deep hollows of complex shapes and recesses, and effective elimination of side-products of vacuum carburizing of steels such as soot and tar with carbon carrier consumption reduced even twice.

On the other hand, high degree of hydrocarbons decomposition reduces considerably the creation of by-products, e.g. soot and tar, and the entire stream of carbon is efficiently transferred to the charge surface.

One of possible implementations of the mixture for under-pressure carburizing according to the present invention is illustrated by the following examples, while the surfaces of the samples are shown in the figure enclosed.

### Example 1

A furnace chamber of the size 200x200x400 mm was charged with workpieces made of low carbon steel grades together with three samples made of 16CrMn5 with deep, narrow hollows of complex shapes. The total surface area of the charge was 0.4 m<sup>2</sup>. After heating under vacuum up to 950°C the carbon carrier was introduced - comprising acetylene and ethylene in the volume ratio 1.0, mixed with hydrogen in the volume ratio 1.17 - with constant flow rate 190 l/hr and pressure pulse was generated in the furnace chamber within the range of 3 to 8 mbar. Steel workpieces were heated 20 minutes under this atmosphere at the temperature of 950°C, then under vacuum for 10 minutes and they were then cooled down to the ambient temperature. On entire surface of the samples including the entire cross section of the deep complex shape hollow, formation of the carburizing layer was found. The layer was of a uniform perlitic structure without precipitation of

secondary carbides and of a uniform depth of  $0.44 \pm 0.05$  mm measured according to the limit structure of 50% perlite and 50% ferrite. No evidence of soot and tar was found either on the surface of carburized workpieces or in the furnace chamber interior.

### Example 2

A furnace chamber of the size 200x200x400 mm was charged with workpieces made of low carbon steel grades together with three samples with made of 17CrNi with deep, narrow hollows of complex shapes. The total surface area of the charge was  $0.4 \text{ m}^2$ . After heating under vacuum up to  $950^\circ\text{C}$  the carbon carrier was introduced - comprising acetylene and ethylene in the volume ratio 0.55, mixed with hydrogen in the volume ratio 1.45 - with constant flow rate 208 l/hr and pressure pulse was generated in the furnace chamber within the range of 3 to 8 mbar. Steel workpieces were heated 20 minutes under this atmosphere at the temperature of  $950^\circ\text{C}$ , then under vacuum for 30 minutes, and then fast cooled to the ambient temperature under 6 bar nitrogen pressure. On the surface of all the samples including the entire cross section of the deep complex shape hollow, formation of the carburizing layer was found. The layer was of a uniform martenzitic structure without precipitation of secondary carbides and of a uniform depth of  $0.46 \pm 0.05$  mm measured according to the minimum limit hardness of 500 HV<sub>0.1</sub>. No evidence of soot and tar was found either on the surface of carburized workpieces or in the furnace chamber interior.

### Example 3

In a furnace with chamber of the size 200x200x400 mm six vacuum carburizing processes with various carburizing mixtures were performed. In each process the carbon carrier comprised acetylene and ethylene was additionally mixed with hydrogen. Composition and proportions of used A, B, C, D, E, F carburizing mixtures are shown in Table 1. In each six processes charge consisted of

workpieces made of low carbon steel 17CrNi with deep with the total surface area of 0.4 m<sup>2</sup>. After heating under vacuum up to 950°C the carburizing mixture was introduced at constant pressure of 5 mbar for 20 min. During this time samples of gas leaving furnace chamber were taken and checked for chemical composition on a mass spectrometer. Afterward the charge was heated under vacuum, and then cooled to the ambient temperature. Results of spectrometric measurements representing decomposition of acetylene and ethylene are shown on the Figure No 2. In the processes D and E intensive effect of synergy of accelerated decomposition of acetylene in presence of ethylene and hydrogen was observed. No evidence of soot and tar was found in the furnace chamber interior while the carbon carrier consumption was reduced over twice comparing to the process C. Uniform carburized layers were found on all external and internal surfaces of all carburized parts.

#### Example 4

While acting as in example 2, the heating of workpieces under vacuum up to the temperature of 905°C is followed by the introduction of the carbon carrier containing acetylene and ethylene in the volumetric proportion of 0.66, mixed with ammonia in the volumetric proportion of 1.1. The mixture is introduced at the constant rate of 140 l/hr, while the pressure inside the chamber is kept pulsating within the range between 3 and 8 mbar. Steel workpieces are heated in this atmosphere at the temperature of 905°C for 20 minutes, and in vacuum for 30 minutes, and then, fast cooled to room temperature under 6 bar nitrogen pressure. On entire sample surfaces, as well as on entire cross-section of deep opening of a complex shape formation of carburized layer was found. The layer was of uniform martensitic structure, without secondary carbide precipitate, characterized by uniform thickness of 0.39 +/- 0.05 mm, determined according to the criterion of minimum limit hardness - 500 HV<sub>0.1</sub>. No evidence of soot and tar was found either on the surface of carburized workpieces or in the furnace chamber interior.

**PATENT CLAIMS:**

1. The mixture for under-pressure carburizing employing the two-component carbon carrier in form of unsaturated hydrocarbons, sometimes mixed with hydrogen and ammonia, is characterized in that it ensures the decomposition of 70% to 90% of hydrocarbons and such as mixture consists of the carbon carrier, containing acetylene and ethylene, while the acetylene to ethylene ratio is within the range between 0.5 and 2.0, while the carbon carrier is also mixed with hydrogen and ammonia.
2. The mixture for under-pressure carburizing according to claim 1 is characterized in that the said carbon carrier is mixed with hydrogen in the proportion from 0.7 to 1.6.
3. The mixture for under-pressure carburizing according to claim 1 is characterized in that the said carbon carrier is mixed with ammonia in the proportion from 0.7 to 5.0.

## Hydrocarbon gas mixture for the under-pressure carburizing of steel

The object of the present invention relates to a mixture used in vacuum furnaces for under-pressure carburizing of steel products, mainly parts of machines, vehicles and all sorts of mechanical apparatuses.

From the US Patent 5,702,540 a process is known, in which a charge is processed under vacuum in the presence of a carbon carrier which consists of unsaturated aliphatic hydrocarbons, where the pressure in the chamber shall not be higher than 1 kPa.

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The patent EPO 0,882,811 is also known in which the carbon carrier is a hydrocarbon with a strict 1:1 carbon-to-hydrogen ratio.

To obtain the required carburizing result the carbon carrier, ethylene or acetylene, is introduced to a hot vacuum furnace chamber during the carburizing stage either in a continuous or a pulse manner. The carbon carrier can be introduced together with other chemically inert gases, e.g. nitrogen, argon, or active gases, e.g. hydrogen, in order to control the efficiency and cleanliness of the carburizing process, as well as with active nitrogen carriers, e.g. ammonia, for carbonitriding of steel.

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Moreover, the carbon carrier is mixed with hydrogen or with ammonia. In the case of mixing the carbon carrier with hydrogen, volume ratio 0.7 to 1 should be maintained. For ammonia this ratio is 0.7 to 5.0.

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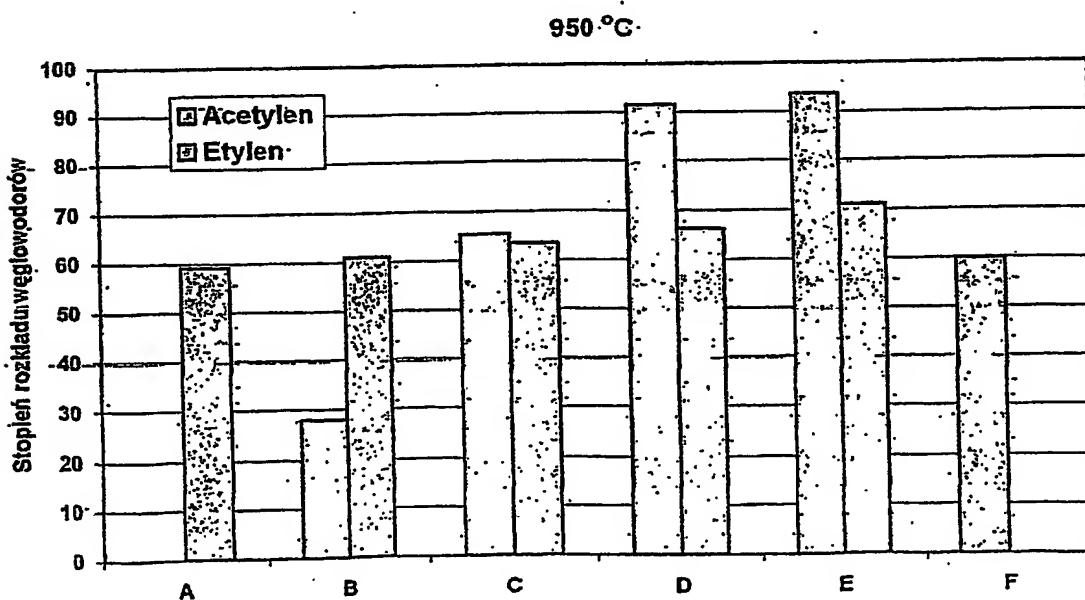
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3. The mixture for under-pressure carburizing according to claim 1 is characterized in that the said carbon carrier is mixed with ammonia in the proportion from 0.7 to 5.0.

## Compositions and proportions of investigated carburizing mixtures.

Composition of the mixture [%]						
Process	A	B	C	D	E	F
Acetylene	0	5	13	23	27	40
Ethylene	80	70	55	33	27	0
Hydrogen	20	25	32	44	46	60
Acetylene and ethylene ratio in carbon carrier	0	0.07	0.23	0.69	1.0	$\infty$
Hydrogen to carbon carrier ratio in the mixture	4.0	3.0	2.13	1.27	1.17	0.66
Carbon carrier consumption l/min.	266	215	166	76	70	62
Carburizing uniformity in deep hollow (see Fig. 1)	-	+/-	+	+	+	+
Charge cleanliness after process	+	+	+	+	+	-

## Degree of decomposition of the carbon carrier components in the carburizing mixtures



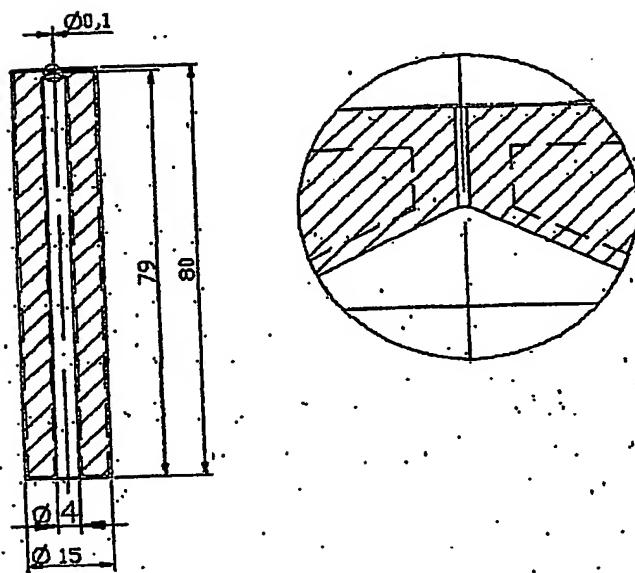
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Shape and sizes of the carburizing sample



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